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AR 201- 12936

January 29, 2001

Administrator
US Environmental Protection Agency
PO Box 1473
Merrifield, VA 22116

Attention: Chemical Right-to-Know Program

Dear Administrator:

Please find enclosed a Microsoft Word document Test Plan for Spent Pulping Liquor (CAS No. 66701-92-9) being submitted for the HPV Challenge Program, AR-201, on behalf of the American Forest & Paper Association HPV Work Group (Consortium Registration #

If you have any questions regarding the Test Plan, please call me at 202/463-2587 (Fax: 202/463-2423; e-mail: John_Festa@afandpa.org).

Sincerely,

John L. Festa, Ph.D
Senior Scientist

Enclosure

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MR 43852

AR 201-12936A

HIGH PRODUCTION VOLUME (HPV)
CHEMICAL CHALLENGE PROGRAM

TEST PLAN

for

SPENT PULPING LIQUOR

CAS No. 66071-92-g

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Submitted to the US EPA for Review and Public Comment

BY

**The American Forest & Paper Association
HPV Work Group**

Consortium Registration #

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Spent Pulping Liquor Test Plan

Plain English Summary

AF&PA is sponsoring the HPV chemical, “sulfite liquors and cooking liquors, spent” (CAS No. 66071-92-g) (commonly referred to as “spent pulping liquor”). Spent pulping liquor is a byproduct of processing (or “cooking”) wood chips to remove the wood pulp to manufacture paper. The vast majority of spent pulping liquor is recycled for chemical or energy recovery at the production site. Spent pulping liquor may be traded between mills for these uses. A limited number of facilities transfer spent pulping liquor off-site for use in other processes. Exposure to humans or the environment is not expected to occur, except in cases of accidental release.

Spent pulping liquor is a complex mixture. It is corrosive, with a pH ranging from approximately 11.5 to 13.5. Spent pulping liquor is classified as a corrosive liquid under Department of Transportation regulations and labeled as such.

The composition of the complex mixture known as spent pulping liquor is highly variable, depending on several factors. These factors include the process and wood species used to manufacture the wood pulp, the type of end product for which the pulp is intended, the composition of the cooking liquor, and the type of digester equipment used in pulping. After reviewing volume, commercial use, and potential for human and environmental exposure from each pulping process, strong black liquor from an elemental-chlorine-free kraft process using a mixture of hardwood and softwood was selected as the most appropriate test material. More detailed justification for selection of this material is presented in the test plan.

While information is available about the chemistry and certain characteristics of spent pulping liquor, including its pH, there are essentially no data available on the required HPV/SIDS endpoints for spent pulping liquor. (Thus, there are no robust summaries accompanying this proposed test plan.) The lack of test data is not surprising in view of the corrosiveness of spent pulping liquor and that it is a byproduct that is almost always recycled at the production site and has only limited commercial use. Moreover, there is no analytical method for measuring spent pulping liquor given that it is a complex mixture of hundreds of different constituents.

Although the likelihood of human or environmental exposure to spent pulping liquor is extremely low, **AF&PA** has carefully reviewed the HPV test battery to determine whether these tests can and should be performed. The test plan explains in detail the following conclusions:

Physicochemical Properties

- AF&PA will test the boiling point and vapor pressure of spent pulping liquor.
- Data on the pH of spent pulping liquor is already available.
- Determination of the melting point is not applicable because the material is a liquid.
- Certain physical and chemical property tests (water solubility, octanol-water partitioning coefficient, pKa and adsorption/desorption to soil) were designed for single pure materials and will not yield valid results given the complexity of the spent pulping liquor mixture. Hence, it is impossible to obtain a single value representing the nature of the mixture from a range of values from the many constituents of this mixture. These tests therefore will not be performed. In addition, none of these endpoints can be measured since an analytical method for spent pulping liquor is not available.

Environmental fate

- Testing for photodegradation requires measurement of the degradation products of the test material. This test cannot be undertaken because the complexity of the spent pulping liquor mixture is such that an analytical method for spent pulping liquor is not available.
- With respect to biodegradation, the caustic nature of the test material would adversely affect the bacteria in a biodegradation test before degradation could occur. However, the test protocol allows for neutralization. It is likely that neutralization will alter the composition of the material, and thus the test would have questionable relevance. However, because this test can be performed, AF&PA will undertake the biodegradation test.
- Hydrolysis as a function of pH testing is designed to test pure substances at environmentally relevant pH levels from 4-9. This test does not apply to spent pulping liquor because it is an alkaline, complex mixture. In addition, this endpoint cannot be measured since an analytical method for spent pulping liquor is not available.

Ecotoxicity

- Tests of aquatic toxicity (fish and invertebrates) and toxicity to algae will be performed on spent pulping liquor. In order to conduct these tests, the test substance will have to be neutralized, which will change the composition of the test material, because different constituents will precipitate out of solution at different pH levels. Thus, the results are likely to be of limited relevance. Nevertheless, AF&PA will undertake the tests because OECD guidelines contemplate testing under neutralized conditions, and because aquatic testing

can be performed without issues of animal welfare that apply to tests using warm-blooded animals.

Health Effects

- Spent pulping liquor is very alkaline in nature, with a pH ranging from 11.5 to 13.5. It is known that exposure to highly corrosive materials induces pain in both humans and animals. Corrosive materials can cause severe ulcerations or necrosis (cell death) at the point of contact, i.e., the esophagus or gastric mucosa (stomach lining) when the test material is administered orally.
- OECD guidelines provide that testing that causes pain in laboratory animals as a result of corrosive effects should not be undertaken. Recent OECD and EPA statements support this conclusion, and the Animal Welfare Act similarly proscribes testing that inflicts pain on animals. Dilution of spent pulping liquor in order to perform the tests would alter the fundamental nature of the test material, as different constituents precipitate out of the solution at different pH levels. Accordingly, mammalian testing with spent pulping liquor will not be conducted.
- In any event, the results of any mammalian testing would be related to the well established, but non-specific corrosive effects of high pH compounds. Ample data exist on other compounds to document the effects of high pH on humans and animals. For this reason, mammalian testing of spent pulping liquor is unnecessary.
- **AF&PA** will conduct in vitro (test tube) genotoxicity testing on spent pulping liquor. It will be necessary to neutralize the test material in order to bring it to a pH that is compatible with survival of the test organisms in order to perform the testing. This will affect the composition of the material and the results therefore may not represent the original substance. However, **AF&PA** will undertake the testing in the spirit of the HPV program.

AF&PA will proceed with the proposed testing -- including boiling point, vapor pressure, biodegradation, ecotoxicity (fish, aquatic invertebrates and algae) and *in vitro* genotoxicity -- following receipt of and response to public comments. Given that no mammalian testing will be performed, there is no need to defer the proposed testing program.

List of AF&PA HPV Consortium Members

The American Forest & Paper Association HPV Consortium includes the following companies:

Abitibi Consolidated
Alliance Forest Products
Blue Ridge Paper Products
Boise Cascade Corporation
Bowater, Inc.
Buckeye Technologies, Inc.
Eastern Pulp and Paper, Inc.
Finch, Pruyn & Company, Inc.
Georgia-Pacific Corporation
Greif Bros. Corporation
Gulf States Paper Corporation
Inland Paperboard and Packaging Company
International Paper Company
Longview Fibre Company
Louisiana-Pacific Corporation
Mead Corporation
P.H. Glatfelter Company
Packaging Corporation of America
Port Townsend Paper Corporation
Potlatch Corporation
Rayonier
Rivet-wood International Corporation
Smurfit-Stone Container Corporation
St. Laurent Paperboard Inc.
Stora Enso North America
Westvaco Corporation
Weyerhaeuser Company
Willamette Industries, Inc.

Spent Pulping Liquor Test Plan

I. Description of Spent Pulping Liquor and Rationale for Selection of Test Material

AF&PA is sponsoring the HPV chemical, “sulfite liquors and cooking liquors, spent” (CAS No. 66071-92-g). This CAS number, also referred to as “spent pulping liquors,” includes the liquors resulting from a variety of pulping processes within the pulp and paper industry.¹ Such processes include kraft, soda, sulfite, semichemical, and chemi-thermomechanical.

Almost all of the spent pulping liquor generated by any of these processes is recycled for chemical and energy recovery. Controlled management of the material minimizes any potential for human or environmental exposure from these activities.

Spent pulping liquor is variable in its composition, depending upon the wood species used to manufacture the wood pulp, the composition of the cooking liquor, and the type of digester equipment used in pulping, and the type of end product for which the pulp is intended. Using Agency guidance, AF&PA has selected strong black liquor from the kraft process at an elemental-chlorine-free mill using a mixture of hardwood and softwood as its test material for the HPV program, as described further below.

EPA guidance suggests that testing the substance produced at the highest volume would be appropriate. (EPA Guidance, *Guidance for “What to Test” for the WV Challenge*, draft dated 2/08/99.) Agency guidance also suggests that the selected test material should be “representative” of the sponsored CAS number. Strong black liquor from a bleached, elemental-chlorine-free (ECF) kraft process using a mixture of hardwood and softwood is most representative of spent pulping liquor in the pulping industry for several reasons:

¹ Spent pulping liquors are defined as:

the aqueous solution resulting from the reaction of lignocellulosic substances (wood or other agricultural fiber sources) with one or more pulping chemicals including those used in the kraft, sulfite, semichemical or other pulping processes. Composition is highly variable and includes excess pulping chemicals, dissolved and degraded cellulose, hemicellulose and lignin.

Volume – The kraft pulping process is by far the most significant process. Annual pulp production capacity from the kraft process is over 57 million tons. Annual pulp production for the other processes fall well below this, in the range of 1-5 million tons per year. Consequently, there is more spent liquor generated by the kraft process than by all other processes combined.

Potential for Human/Environmental Exposure – Virtually all spent pulping liquor of any kind is recycled for chemical and energy recovery. The vast majority thus remains on-site, with two very minor exceptions.

- An extremely small percentage of spent pulping liquor is transferred via pipeline to adjacent plants for lignin extraction or dimethyl sulfide extraction. Remaining spent pulping liquor is then returned to the pulp mill to be recycled for chemical and energy recovery.
- Strong black liquor may be transported by truck to other pulping facilities that use it for chemical and energy recovery.

While potential for exposure to spent pulping liquors is minimal, accidental spill within a mill or during transportation represents the most plausible source of environmental exposure. (When black liquor is recycled or transported, some water is typically removed, and the material is therefore referred to as “strong black liquor.” Strong black liquor has higher pH than weak black liquor, and thus would be expected to be on the higher end of the range given in Material Safety Data Sheets for black liquor.)

Representative of Industry Practice – Kraft black liquor from a pulping process using a mixed blend of hardwood and softwood, and elemental chlorine free (ECF) bleaching is most representative of current industry practices. Most mills produce both softwood and hardwood pulp at a single location. Spent pulping liquor most often exists as a blend from processing both hardwood and softwood. In addition, United States production of bleached pulp is greater than unbleached pulp, and ECF is the technology basis for recent water regulations for bleached kraft pulp mills.

Accordingly, the material to be used for testing of spent pulping liquor will be spent strong black liquor taken from an ECF bleached kraft mill that uses a mixture of hardwood and softwood. This will provide the most appropriate material to represent CAS No. 66071-92-9, spent pulping liquor.

II. Chemical Composition of Spent Pulping Liquor

A. Kraft Black Liquor Composition

Strong black liquor contains between 50 and 70% solids, with the remainder being water. The solids are comprised of a complex mixture of both inorganic and organic constituents.

1. Inorganic Constituents

The inorganic constituents in black liquor are derived from the cooking liquor which is used to pulp the wood chips, and are comprised of sodium hydroxide (NaOH), sodium sulfide (Na_2S), sodium carbonate (Na_2CO_3), sodium sulfate (Na_2SO_4), sodium thiosulfate, ($\text{Na}_2\text{S}_2\text{O}_3$), and sodium chloride (NaCl). Collectively, inorganic salts constitute between 18 and 25% of the solids in black liquor.

2. Organic Constituents

The organic compounds found in black liquor are derived from wood. They are either 1) natural wood extractives (or their reaction products) that are released as a result of the pulping process, or 2) materials formed through the reactions of the pulping liquors with the lignin or cellulose components of wood. Therefore, the compounds can be classified as lignin derived, cellulose derived, or extractives derived. Typical content ranges in kraft liquor are:

- Lignin derived (39-54%; primarily consisting of polyaromatic macromolecules with lesser amounts of low molecular weight alcohols, aldehydes and simple phenolic compounds such as phenol, p-methyl phenol, catechol and guaiacol),
- Cellulose derived (25-35%; primarily a mixture of carboxylic acids such as formic, acetic, glycolic, lactic and glucoisosaccharinic), and
- Extractive derived (3-5%; primarily resin acids and fatty acids which are converted to salts at the high pH of the mixture).

In sum, spent pulping liquor can have hundreds of constituents.

B. Acid-Base Properties of Black Liquor

Black liquor is distinctly alkaline (caustic), with Ph ranging from 11.5 to 13.5 (Various company Material Safety Data Sheets.) Due to the presence of three distinct buffer systems, black liquor is highly buffered. These buffer systems, and their pKa values (representing their potential for dissociation) are:

Sulfide buffer: $\text{Na}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{NaHS} + \text{NaOH}$ pKa \cong 13-13.5

Phenolic buffer: $\text{R-OH} + \text{NaOH} \rightarrow \text{R-ONa} + \text{H}_2\text{O}$ $\text{pKa} \approx 9.4\text{--}10.8$

Carbonate buffer: $\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{NaHCO}_3 + \text{NaOH}$ $\text{pKa} \approx 10.2$

The high alkalinity is largely responsible for solubilizing the various organic constituents. If the pH is reduced, various organic constituents will precipitate, beginning with the components with low pKa values (e.g. the phenolics) and eventually those with higher pKa values (e.g. the carboxylic acids). Thus, the soluble component would vary as pH is reduced. Consequently, if the pH is adjusted in order to perform certain tests, the nature and composition of the test material will necessarily change.

C. Lack of Analytical Method

There is no analytical methodology available to measure spent pulping liquor. Spent pulping liquor is a mixture of numerous known, tentatively identified and unidentified components, and thus only some components would be available for calibration purposes. Given the complexity of the mixture, it is not currently possible to characterize spent pulping liquor as necessary to undertake a number of the SIDS endpoints. The HPV program does not encompass the kind of research program that would be necessary in order to develop an appropriate analytical method with sufficient sensitivity, if indeed it is even possible to do so. Consequently, because of the lack of an appropriate analytical methodology and the practical impossibility of developing such a method, many of the required SIDS endpoints that are part of the HPV Challenge program cannot be undertaken.

III. Review of Existing Data and Development of Test Plan Rationale for SIDS Endpoints

A. Physicochemical Data

Except for pH, physicochemical data for spent pulping liquor that satisfy the data evaluation criteria described in EPA guidance documents were not found. Most of the required physicochemical properties tests in the SIDS battery are designed for a single, pure chemical. Due to the fact that spent pulping liquor is an extremely complex mixture of inorganic and organic constituents, many of the common physicochemical parameters are inapplicable.

If one were to attempt these tests, the numerous different constituents in spent pulping liquor will respond to most physicochemical tests differently. The resulting wide ranges of values for the individual constituents would not represent the characteristics of the mixture.

The problem is further exacerbated by the lack of a suitable analytical procedure to measure spent pulping liquor. Absent a suitable analytical method for

measuring the spent pulping liquor, some of the tests cannot be performed. For these reasons, many of the **SIDS physicochemical** tests in this category cannot be performed or would not produce useful **pKa** information. Tests that are inappropriate for this material include **pKa**, water solubility, octanol-water partitioning coefficient (K_{ow}), and **adsorption/desorption** to soil. AF&PA will test the boiling point and vapor pressure of spent pulping liquor. Data on pH of spent pulping liquor are already available, and determination of the melting point is not necessary since the material is a liquid. The following narrative explains the rationale for this testing plan in more detail.

1. **Water Solubility**

Spent pulping liquor is a complex mixture of inorganic and organic salts suspended or dissolved in water. A test for water solubility could be performed on the test material, but it would result in multiple values for individual constituents. Due to the lack of a suitable analytical method for the complex mixture, it is not feasible to measure the water solubility for the mixture.

As noted above, strong black liquor contains **50-70%** solids. At solids contents below **50%**, the inorganic salts contained in spent pulping liquor are completely dissolved in the aqueous portion of the liquor. Often, the 50% solids point (the point where the salts start precipitating) is referred to as the “solubility limit.” At solids levels greater than **75%**, Burkeite ($2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$) is the only salt that precipitates. Thus, between 50 to 75% solids, spent pulping liquor is essentially a water/organic-inorganic suspension (Adams et al. 1997).

2. **Melting Point and Boiling Point**

Because spent pulping liquor is a liquid under normal conditions, it is not necessary to determine the melting point. However, **AF&PA** will test to determine the boiling point.

3. **Octanol:Water Partition Coefficient**

Given the numerous organic and inorganic constituents in kraft black liquor, any assay used to estimate the partitioning properties would yield a range of values reflecting this complex mixture. Such values would be meaningless and would provide little, if any, useful information concerning the material. Consequently, the K_{ow} will not be conducted on this mixture.

4. **pH**

Already available data show that the pH of kraft black liquor ranges from 11.5 to 13.5 (various company Material Safety Data Sheets).

5. **pKa**

Because **pKa** determinations apply to specific compounds, this endpoint cannot be conducted on spent pulping liquor, which is a complex mixture.

6. Adsorption/Desorption to Soil

Due to the fact that black liquor is an extremely complex mixture of inorganic and organic constituents, the test for **adsorption/desorption** to soil would have little, if any, meaning. The different constituents will **adsorb/desorb** to soil differently, resulting in a wide range of values. Moreover, because there is no analytical method for the spent pulping liquor mixture, the adsorption/desorption to soil of spent pulping liquor will not be determined.

7. Density

The density of spent pulping liquor will be determined.

Summary: The boiling point, vapor pressure, and density of kraft black liquor will be determined. Data are already available on pH. Testing will not be conducted for pKa, water solubility, octanol-water partitioning coefficient, or adsorption/desorption to soil.

B. Environmental Fate & Pathways

Data on environmental fate for spent pulping liquor that satisfy the data evaluation criteria described in EPA guidance documents were not found. Described below is the feasibility of conducting the required **SIDS** testing for the fate and transport endpoints.

1. Photodegradation

The practicability of performing this test is hindered by the lack of an analytical procedure to measure spent pulping liquor. A test of photodegradation cannot be performed, since the composition and quantity of the test material before and after exposure to sunlight cannot be measured.

2. Hydrolysis

With respect to the hydrolysis test, the required test (OECD 111) is designed to measure hydrolysis (stability in water) of pure compounds at several **pH** levels (4-9) that are likely to be found in the environment. Thus, the test is not applicable to the alkaline, complex mixture of spent pulping liquor. In addition, this endpoint cannot be measured since an analytical method for spent pulping liquor is not available.

3. Biodegradation

An additional problem is presented for biodegradation testing. The high pH of the test material would not be compatible with survival of the bacteria, thus preventing the possible degradation of the material. However, the test guidelines allow neutralization of materials in order to conduct this test. While neutralization will alter the composition of the test material because various constituents will precipitate out as the pH changes, the test can be performed. An analytical method for spent pulping liquor is not necessary. AF&PA therefore proposes to conduct biodegradation testing, even though the results must be interpreted with caution.

Summary: Due to the complex nature of spent pulping liquor and the attendant lack of a practical analytical methodology for spent pulping liquor, the hydrolysis and photodegradation tests cannot be performed. Biodegradation testing will be performed after the test material is neutralized, although results will likely be of limited relevance.

C. Ecotoxicity Tests

Data on the SIDS ecotoxicity endpoints (acute toxicity to fish and aquatic invertebrates and toxicity to plants) that satisfy the data evaluation criteria described in EPA guidance documents were not found for spent pulping liquor.

The Animal Welfare Act does not apply to the aquatic test organisms. However, each of the ecotoxicity endpoints must be tested within a narrow pH range (6.5 to 8.5), consistent with maintaining the viability of the test organisms. Due to the high pH of black liquor (i.e., approximately 11.5 to 13.5), the only way that ecotoxicity tests could be conducted would be to neutralize test solutions to the lower pH range.

The latest OECD (#203) guideline suggests that adjustment of the pH with simple acid or alkali (or other suitable buffer) can be done, even though *"this can cause sedimentation and/or degradation of the test substance."* Adjustment of the pH can be carried out in the stock solution or in the media itself, as judged appropriate.

However, in the particular case of spent pulping liquor there is a further complication. Reducing the pH to levels at which the test organisms survive will effectively alter what is in solution. Consequently, whatever constituents remain in the aqueous phase, the resulting mixture would no longer be representative of spent pulping liquor.

Nevertheless, even though the "neutralized" material would not be representative of the chemical CAS number being tested, it could potentially represent a situation in which a spill of the very caustic material is diluted to a lower pH by virtue of accidental discharge into a large water body. Such a scenario is

unlikely. The resulting data would be of limited relevance. However, the test can be accomplished, and OECD guidelines contemplate using neutralized test materials.

Thus, even though the relevance of the results will be highly limited with respect to the potential ecotoxicity of spent pulping liquor, the **SIDS** ecotoxicity endpoints will be determined to fulfill the spirit of the HPV program.

Summary: Following appropriate adjustments of the pH of spent pulping liquor, this material will be tested for toxicity to fish, daphnia, and algae consistent with the required SIDS ecotoxicity endpoints. Data should be interpreted with caution, however.

D. Human Health Effects

Data on the **SIDS** human health effects endpoints of acute toxicity, genetic toxicity, repeat dose toxicity, reproductive and developmental toxicity for spent pulping liquor that satisfy the data evaluation criteria described in EPA guidance documents were not found.

However, with the exception of the in *vitro* tests for mutagenicity in Salmonella bacteria and mammalian cells, all of the other human health effects endpoints require the test substance to be administered to animals either by gavage or in the diet. The high pH of the test material in this case would result in immediate corrosive effects in the animals. Not only would useful mammalian toxicity data not be obtained, but the spirit of the HPV program requires that testing in which animals would suffer should not be conducted. Therefore, AF&PA will limit health effects testing to the mutagenicity endpoints and not perform mammalian toxicity tests for spent pulping liquor.

1. Likely Corrosive Effects

Given the extremely high pH of kraft black liquor (approximately 11.5-13.5), it would be impossible to administer such a caustic material to test animals without causing them to suffer. It is well established that highly alkaline material can cause chemical burns. *‘Extremely corrosive and reactive chemicals may produce immediate coagulative necrosis that results in substantial tissue damage. . . .’* (Casarett & Doull 1997) As a leading occupational medicine text notes: *“Alkalis not only coagulate tissue protein by dessication or salt formation, but they a/so saponify fats and cause liquefaction necrosis.”* (Zenz 1994) The severity of the effect will depend on the corrosiveness of the chemical. (Olishifski 1974). OECD’s Guidance Document on the Recognition, Assessment, and Use of Clinical Signs as Humane Endpoints for Experimental Animals Used in Safety Evaluation provides that *“If something is known to cause suffering in humans, it should be assumed to cause suffering in animals.”* (OECD 2000).

With a pH in the range of 11.5 to 13.5 (and with the strong black liquor test material generally expected to be at the higher end of this range), spent pulping liquor is clearly corrosive. When shipped, spent pulping liquor is labeled as corrosive (UN1 760 label) under Department of Transportation regulations. Manufacturers of spent pulping liquor comply with OSHA's Hazard Communication Standard, including providing Material Safety Data Sheets for the material. (OSHA defines as corrosive and therefore hazardous those chemicals that cause visible destruction of tissue at the site of contact. (Code of Federal Regulations, OSHA). EPA automatically defines waste as hazardous due to the characteristic of corrosivity if the pH of the material is 12.5 or higher. (Code of Federal Regulations, EPA).

Thus, based on well-known characteristics of any corrosive material, one would expect spent pulping liquor to result in chemical burns. Whether by gavage or via administration in the diet, the high pH of spent pulping liquor is expected to cause severe ulcerations or necrosis at the point of contact, i.e., esophagus or gastric mucosa, when fed to test animals.

2. Pertinent OECD Testing Guidelines

OECD guidelines provide that testing not be carried out when it will cause distress to the animals based on corrosive effects of the test substance:

- As noted in the guidelines for acute toxicity testing (OECD 401), "Dosing test substances in a way known to cause marked pain and distress due to corrosive or irritating properties need not be carried out." Indeed, OECD is currently taking steps to eliminate acute (LD_{50}) testing in light of animal use concerns.
- OECD 420 on acute toxicity further notes that, "doses that are known to cause marked pain and distress, due to corrosive or severely irritant actions, need not be administered."
- Moreover, OECD 422 governing repeat-dose testing provides: "*The highest dose /eve/ should be chosen **with** the aim of inducing toxic effects but not death nor obvious suffering.*" [Emphasis added] It is not clear that these dual requirements can be satisfied simultaneously with such a corrosive material.

For spent pulping liquor, even small doses would likely result in "*obvious suffering*" of the test animals.

3. Animal Welfare Act and Other Licensing Provisions

The Animal Welfare Act, 7 U.S.C. § 2131, requires that the Secretary of Agriculture set standards governing the humane handling, care, treatment, and transportation of animals by research facilities. The standards should ensure that experimental procedures *"ensure that animal pain and distress are minimized, "* and that the investigator considers *"alternatives to any procedure likely to produce pain to or distress in an experimental animal. "*

The regulations are found at 9 C.F.R. Ch. 1. Generally, they require each research facility to ensure that its activities *"avoid or minimize discomfort, distress, and pain to the animals."* 9 C.F.R. § 2.31(d)(i). In its annual report, the research facility must certify that each principal investigator has considered alternatives to *"painful procedures,"* (9 C.F.R. § 2.36), defined as *"any procedure that would reasonably be expected to cause more than slight or momentary pain or distress in a human being to which that procedure was applied, that is, pain in excess of that caused by injections or other minor procedures."* 9 C.F.R. § 1.1

The Animal Welfare Act thus requires that testing that inflicts pain on the animals is to be carefully scrutinized.

4. Evaluation of Test Feasibility

Applying OECD guidelines and observing relevant provisions for animal welfare, it does not appear that animal testing of spent pulping liquor can reasonably be conducted.

At the pH of this material, primary toxicity is related to the inherent corrosivity of the material. Some of the pertinent OECD test guidelines allow for dilution of the test material used for animal testing. However, in the case of spent pulping liquor, dilution would alter the composition of the material. Thus, the tests of a dilute substance would be addressing a different material - both in composition and because the fundamental corrosive property of the material has been changed. Relevance of testing with such a fundamentally altered substance is highly questionable (and even less potentially applicable than aquatic testing with dilute material). Given the strictures applicable to testing warm-blooded animals, mammalian testing with spent pulping liquor should not be performed.

5. EPA Guidance

The latest guidance from EPA (2000) states: *"In analyzing the adequacy of existing data, participants shall conduct a thoughtful, qualitative analysis rather than use a rote checklist approach. Participants may conclude that there is sufficient data, given the totality of what is known about a chemical, including human experience, that certain endpoints need not be tested."*

Given the high pH and corrosivity of this complex mixture, a thoughtful analysis leads to the conclusion that mammalian testing of spent pulping liquor cannot be justified.

6. In Vitro Genotoxicity Testing

The potential for in vitro genotoxicity will be tested in *Salmonella* and a *mamallian cell* culture, recognizing that the pH will have to be adjusted in order to ensure survival of the test organisms.

Summary: Given the high pH of spent pulping liquor and the certainty of causing animal suffering should this material be administered in order to conduct the required tests, none of the SIDS human health endpoints involving the use of animals will be undertaken. However, AF&PA will subject spent pulping liquor to in vitro genotoxicity testing.

References

Adams, T.N., Frederick, W.J., Grace, T.M., Hupa, M., Lisa, K., Jones, A.K., and Tran, H. 1997. Kraft Recovery Boilers, T.N. Adams, Ed. TAPPI Press, Technology Park, P.O. Box 105113, Atlanta, GA 30348.

American Conference of Governmental Industrial Hygienists (ACGIH) 1991. Documentation of the Threshold Limit Values and Biological Exposure Indices, Sixth Edition. Cincinnati, OH.

Casarett & Doull's Toxicology, The Basic Science of Poisons, Klaassen, C. ed. 5th ed. 1996. p 533.

Code of Federal Regulations, OSHA, volume 29, Part 1910.1200, Appendix A, Health Hazard Determinations.

Code of Federal Regulations, EPA, volume 40, Part 261.22, **Characteristic of Corrosivity**.

EPA. Oct. 14, 2000. Letter from Susan Wayland, Deputy Assistant Administrator describing guidelines for limiting the unnecessary use of animals in implementing the HPV Challenge program.

Material Safety Data Sheets from various companies.

Olishifski, J, ed. Fundamentals of Industrial Hygiene (National Safety Council). 1974.

Organisation for Economic Co-operation and Development (OECD). 2000. Guidance Document on the Recognition, Assessment, and Use of Clinical Signs as Humane Endpoints for Experimental Animals Used in Safety Evaluation. Environment Directorate Joint Meeting Of The Chemicals Committee and the Working Party On Chemicals, Pesticides And Biotechnology. Env/JM/Mono(2000)7.

OECD Guideline For Testing of Chemicals, Combined Repeated Dose Toxicity Study with the Reproduction/Developmental Toxicity Screening Test, OECD 422.

OECD Guideline For Testing of Chemicals, Acute Oral Toxicity, OECD 401.

OECD Guideline For Testing of Chemicals, Acute Oral Toxicity - Fixed Dose Method, OECD 420.

Venkatesh, V. and Nguyen, X.N. 1985. Chemical Recovery in the Alkaline Pulp Process, G. Hough, Ed., **TAPPI** Press Technology Park, P.O. Box 105113, Atlanta, GA 30348. Chapter 3. Evaporation of Black Liquor, pp 15-85.

Zenz, C, Dickerson, O., and Horvath, E., Eds. Occupational Medicine, 3d edition (1994).